Electrochemical hydrodehalogenation of polychloromethanes at silver and carbon electrodes

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ABSTRACT

The reductive dehalogenation of CCl_4, $CHCl_3$, CH_2Cl_2 and CH_3Cl has been investigated by cyclic voltammetry and controlled-potential electrolysis at Ag, glassy carbon (GC) and graphite electrodes in dimethylformamide (DMF) + 0.1 M Et_4NClO_4 in the absence and presence of a proton donor. In particular, the study was focused in the evaluation of the intermediates and final products of the reduction process and how their distribution could be affected by tuning relevant chemical and electrochemical parameters. In general, depending on the value of the applied potential, all polychloromethanes (PCMs) can be partially or completely dechlorinated, methane being exclusively formed in the latter case. The nature of the electrode material and the proton availability of the medium affect drastically the distribution of reduction products. The results point out that at both types of electrode, reduction of PCMs takes place through two competing reaction pathways both leading to methane. One reaction route involves a sequence of reductive dehalogenation steps, with the removal of one chlorine atom at a time, whereas the other is based on hydrogenolysis of carbenes and bypasses the intermediacy of partially dechlorinated PCMs. The presence of a proton source affects substantially the hydrodehalogenation efficiency, enhancing the concentration of intermediate PCMs and the final yield of methane. The silver electrode exhibits an extraordinary electrocatalytic effect resulting in remarkable positive shifts of the reduction potentials of all PCMs with respect to GC. The Ag surface strongly affects the kinetics of the dissociative electron transfer to $CH_nCl_{(4-n)}$ ($n = 0$–3) as well as the reactivity of the intermediate radicals, carbanions and carbenes.

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1. Introduction

Chlorinated solvents such as polychloromethanes (PCMs), polychloroethanes, and polychloroethylenes form one of the main groups of environmental pollutants present in the soil and underground waters of many industrial sites [1]. This contamination is particularly dangerous due to the toxic and carcinogenic character of these compounds, worsened by their relatively high solubility in water and hence their great mobility [2].

Many methodologies have been developed for the degradation of water pollutants; these include chemical and photochemical methods such as chlorination, ozonization and ultraviolet irradiation, as well as biological and electrochemical oxidation methods [3]. Although many of these methods are efficient in the abatement of non-halogenated water pollutants, often they are inadequate for the remediation of volatile polychlorinated organic solvents due to the recalcitrant nature of the latter and to the production of secondary pollutants. The conventional methods of removal of these compounds are air-stripping and adsorption on activated carbon, but both involve a simple transfer of the pollutant from one phase to another and, hence, require treatment or appropriate disposal in a second stage. Biological treatment, which is relatively slow and is, therefore, more suitable for the treatment of contaminated soil rather than flowing water, may be inhibited by the toxicity of the organic halides and/or their partially dechlorinated products toward the living microorganisms [4]. Incineration appears to be inadequate because of the low flammability of the compounds and the possibility of formation of more dangerous compounds such as dioxins [5]. On the contrary, reductive methods of organic halides, and the electrochemical one in particular, represent a very promising approach, being intrinsically milder, more selective and easier to run than most of the above mentioned methodologies, despite the significant electrical energy requirement.

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The electrochemical destruction of chlorinated volatile organic compounds (VOCs) has been extensively studied in aqueous solutions at various electrode materials, mainly metals, graphite and composites [5–16]. The reduction of many chlorinated molecules at the most commonly used cathodes occurs at very negative potentials, where concomitant reduction of water may take place, resulting in abundant H_2 generation and a drastic decrease of current efficiency [10]. Therefore, electrode materials with prominent catalytic properties toward the reductive deha- logenation of C–Cl bonds are required. Pd and Pt as well as some high hydrogen overvoltage metals such as Ag, Zn, Pb, Cu, Fe and Ni have been used as electrocatalytic cathodes for the reductive dehalogenation of chlorinated VOCs [5–16]. Although good current efficiencies and almost complete dechlorination can be achieved with many of these catalytic systems, there is a general tendency to gradual passivation of the electrode. Also use of precious metals such as Pd and Pt in large-scale applications is not very attractive for economic reasons.

The electrochemical reduction of chlorinated VOCs has also been investigated in nonaqueous solvents, especially as an environmentally friendly electrosynthetic process [17–22]. Since these compounds are highly soluble in organic solvents, highly concentrated solutions can be prepared and electrolyzed with high current densities. This means that great amounts of chlorinated VOCs may be transformed to less dangerous products in a reasonably short period of time. So far, partial or complete dechlorination of CCl_4 [5,6,17], $CHCl_3$ [18], CH_2Cl_2 [19] and CF_2Cl_2 [20,21] has been reported. This electrochemical method of dechlorination is attractive as a preventive tool to be applied to the destruction of existing stocks of banned chlorinated VOCs or those which are produced as byproducts in some industrial processes. It can also be applied to the treatment of water pollutants once these are extracted from water either by adsorption on activated carbon or by air-stripping.

As in the case of aqueous solutions, electrochemical destruction of chlorinated compounds in nonaqueous solvents requires catalytic electrodes in order to avoid the background electrolyte discharge and to limit, as much as possible, the energy consump- tion [18]. A variety of electrode materials has been investigated, some of them, especially Ag, showing good catalytic properties both in terms of current efficiency and selectivity. In our own experience, Ag possesses extraordinary electrocatalytic properties toward the reduction of organic halides [23,24]. This electro- catalytic process has been intensively investigated from different viewpoints and some crucial aspects of the mechanism are by now well understood [23–28]. So far, however, the electrocatalytic properties of Ag have been exploited mainly for electrosynthetic purposes [29–33], although few environmental applications have also been reported [5,6,34].

Herein, we describe the electrochemical hydrodehalogenation of polychloromethanes, CCl_4, $CHCl_3$, CH_2Cl_2 and CH_3Cl, of general formula $CH_nCl_{(4-n)}$ ($n = 0$–3) in dimethylformamide both at a highly catalytic Ag electrode and at a carbon electrode, which is the best approximation to a non-catalytic surface. Although the electrochemical dehalogenation of chlorinated VOCs has been widely investigated at various catalytic cathodes both in aqueous and nonaqueous solutions, little is known about the mechanism of the electrode process. In particular, when complete dehalogena- tion can be achieved, it is not clear whether the process proceeds by successive removal of chlorine atoms, producing less chlorinated compounds as intermediates or not. This work addresses this issue both at catalytic and non-catalytic surfaces. Since hydrodehalogenation involves both electron and proton transfers, it is helpful to be able to control both of them. To this end, use of an organic solvent with low proton availability appears

to be the best choice for mechanistic investigations. Of course transposition of the results obtained at such a medium to an aqueous solution is not straightforward, but is certainly a good starting point.

2. Experimental

2.1. Chemicals

Dimethylformamide (DMF, Acros Organics, 99%) was treated with anhydrous Na_2CO_3 and doubly distilled at reduced pressure under a N_2 atmosphere. Tetraethylammonium perchlorate (Et_4N-ClO_4) was prepared by mixing equimolar amounts of tetraethy- lammonium bromide (Fluka, >98%) and $NaClO_4$ (Acros, 99+%) in warm ethanol; the salt was recrystallized twice from H_2O and dried in a vacuum oven at 70 °C. Tetra-n-butylammonium perchlorate (Fluka, ≥98.0%) was recrystallized from ethanol/water mixture (2/1) and dried at 60 °C under vacuum. CCl_4, $CHCl_3$, CH_2Cl_2 and CH_3Cl were high purity reagents purchased from Sigma– Aldrich and were used without further purification.

2.2. Electrochemical instrumentation

Electrochemical measurements were performed on a compu- ter-controlled EG&G PARC Model 273A potentiostat equipped with a digital coulometer. Cyclic voltammetry experiments were carried out in a three electrode cell system with a glassy carbon disc or a silver disc as working electrode. The counter electrode and the reference electrode were a Pt wire and $Ag|AgI|0.1$ M n-Bu_4NI in DMF, respectively. The latter was calibrated after each experiment against the ferricenium/ferrocene couple, which in DMF has an E^{θ} value of 0.475 V vs. SCE. The potentials measured against the $Ag|AgI|I^-$ reference electrode were converted to the SCE scale, to which all potentials in the paper are referred. The working electrodes were built from a 3 mm diameter GC rod (Tokai GC-20) or from a 2 mm diameter Ag wire (Alfa Aesar, 99.999%) and were cleaned and activated prior to each experiment as previously described [23]. Controlled-potential electrolyses were carried out in a divided cell using an Ag cylinder of 10 cm^2 area or a graphite rod of 5 cm^2 area as working electrode, a Pt foil as counter electrode and $Ag|AgI|I^-$ as a reference electrode. All experiments were carried out at 25 °C.

2.3. Analytical methods

Electrolysis products in the liquid phase were analyzed as headspace samples after preconcentration by means of solid-phase microextraction (SPME). The analyses were performed on a HP 6890 gas chromatograph equipped with a HP 5973 mass selective detector (MS) and a DB-5 ms 30 m × 0.25 mm × 0.25 μm capillary column (Agilent Technologies, USA). The SPME apparatus and fibers were purchased from Supelco (Supelco Park, Bellefonte, PA 16823-0048, USA). Silica fibers coated with a 75 μm Carboxen polydimethylsiloxane (CX-PDMS) were used in this study. Authentic compounds were used for the identification and quantification of the products. All quantitative determinations were based on calibration curves. A single standard mixture, 10^{-2} M in CCl_4, $CHCl_3$ and CH_2Cl_2, was prepared in DMF containing 0.1 M Et_4NClO_4, and was used as a primary stock solution; standards at different concentrations of polychloromethanes were prepared by appropriate dilution of this stock solution.

Preparation and gas chromatographic analysis of all SPME samples were carried out according to the following procedure. 1 mL of doubly distilled water and 10 μL of either a standard solution or an electrolyzed solution were mixed in a 20 mL vial with

a stir bar; the vial was then capped, dipped in a water bath at 20 °C and magnetically stirred at a rate of 400 rpm. The syringe needle of the SPME apparatus was inserted through the septum cap into the vial and the fiber was exposed in the headspace above the liquid sample. Sampling was performed for 20 min, while the solution was under continuous magnetic stirring [35], then the needle was removed from the vial and inserted into the heated injection port of the gas chromatograph. Desorption of PCMs was carried out at their optimum desorption temperature (300 °C for CX-PDMS) for 3 min. During desorption, the temperature of the analytical column was kept at a low value (35 °C) in order to achieve a focusing effect. The injector was equipped with a 0.75 mm i.d. liner, which enables obtaining good peak shapes, and was operated in a split mode (5:1). The oven temperature was set at 35 °C for 4 min, then increased to 40 °C at a rate of 10 °C min^{-1} and finally to 260 °C at a rate of 30 °C min^{-1}, where it was held for 2 min (total duration ca. 14 min). Even if all components elute under 8 min, a further heating of the column was necessary for the 'cleaning' of the SPME bleeding components. Helium with a flow of 0.8 mL min^{-1} was used as a carrier gas. Each day, a column blank, a fiber blank and a water blank were run to determine the extent of any laboratory contamination. The SPME fibers were preliminarily conditioned at their maximum operation temperature (300 °C) for 1 h at least.

The electrolysis products in the gas phase were analyzed on a HP 6890 system gas chromatograph, equipped with a flame ionization detector (FID) and a HP Plot Q 30 m × 0.537 mm × 0.40 μm capillary column (Agilent Technologies, USA). A sample was withdrawn from the reaction cell with a gas syringe through a septum cap and injected directly into the gas chromatograph. Identification of the products and construction of calibration curves for their quantitative determination were based on a certified gas mixture acquired on purpose. The composition of the mixture (mol%) was methane (2.81), ethylene (2.74), acetylene (2.35), chloromethane (0.926), propylene (0.747) and nitrogen the remnant. The injector was equipped with a 0.75 mm i.d. liner and was operated in a split mode (15:1). The oven temperature was set at 60 °C for 2 min, then increased to 240 °C at a rate of 25 °C min^{-1} and held for 2 min. The injector and the detector were set at 200 and 250 °C, respectively, and the carrier gas flow was 4 mL min^{-1}.

All chromatographic data were acquired and analyzed with a validated HP Chemstation software.

3. Results and discussion

3.1. Cyclic voltammetry

A detailed description of the voltammetric behavior of polychloromethanes, which is quite complicated, especially at Ag, is out of the scope of this paper; it is the subject of a separate paper [36]. Here we will consider only some features relevant to the discussion of the electrolysis experiments. Cyclic voltammograms of CCl$_4$, CHCl$_3$, CH$_2$Cl$_2$ and CH$_3$Cl at glassy carbon (GC), in the absence and presence of acetic acid (HAc), are depicted in Fig. 1. In the presence of acid, each compound exhibits a series of irreversible reduction peaks equaling in number that of the chlorine atoms present in the molecule. If no acid is added into the solution, both CCl$_4$ and CHCl$_3$ show an intense first peak followed by a series of small peaks. The presence of excess acid modifies the intensities of all peaks, which become almost of the same height, but does not modify appreciably the peak potentials. A comparison of the peak potentials measured for each compound with those of the others shows that reduction of each PCM involves the intermediate formation of all less chlorinated compounds. Thus, CCl$_4$ is first reduced to CHCl$_3$, then to CH$_2$Cl$_2$ and then to CH$_3$Cl, which is finally reduced to CH$_4$. Table 1 summarizes
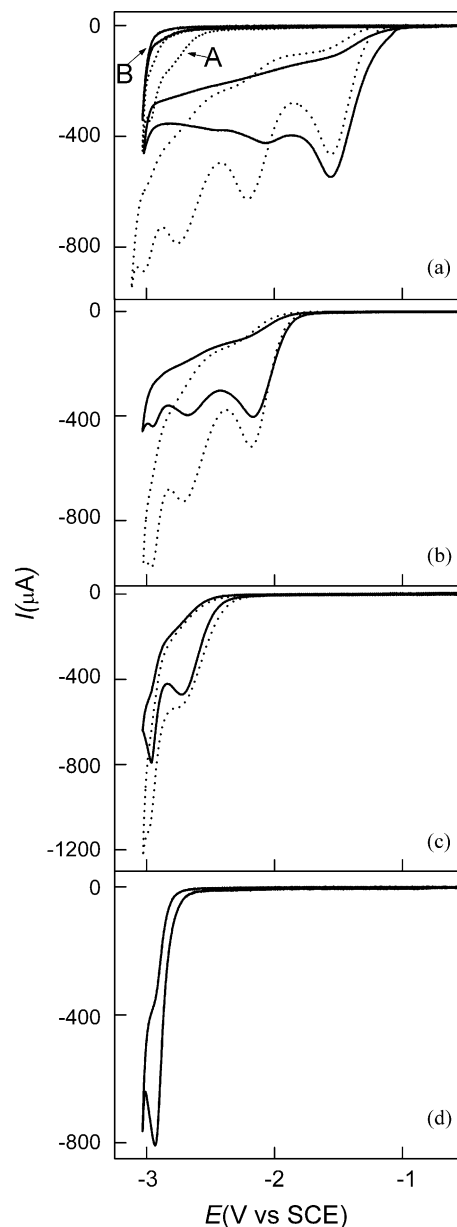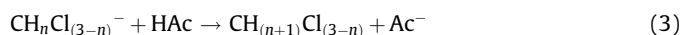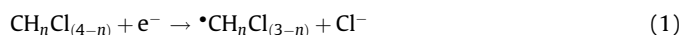

Fig. 1. Cyclic voltammetry of (a) 10 mM CCl$_4$, (b) 10 mM CHCl$_3$, (c) 10 mM CH$_2$Cl$_2$ and (d) 6 mM CH$_3$Cl recorded at $v = 0.2$ V s^{-1} at GC in DMF + 0.1 M Et$_4$NClO$_4$ in the absence (solid line) and presence (dotted line) of 50 mM CH$_3$CO$_2$H; curves (B) and (A) stand for the background electrolyte and 10 mM CH$_3$CO$_2$H, respectively.

the reduction potentials of all four compounds; the peak potential, E_p, of the first reduction process, representing hydrogenolysis of each substrate to the immediately less chlorinated compound, is reported in the table.

Analyses of the voltammetric data obtained in the presence of acetic acid indicate the following reductive cleavage mechanism [36]:

$$CH_nCl_{(4-n)} + e^- \rightarrow {}^\bullet CH_nCl_{(3-n)} + Cl^- \qquad (1)$$

$$^\bullet CH_nCl_{(3-n)} + e^- \rightleftarrows CH_nCl_{(3-n)}{}^- \qquad (2)$$

$$CH_nCl_{(3-n)}{}^- + HAc \rightarrow CH_{(n+1)}Cl_{(3-n)} + Ac^- \qquad (3)$$

where $n = 0$–3. The first step is a concerted dissociative electron transfer (ET), i.e., ET and C–Cl bond rupture occur in a single step.

Table 1
Reduction potentials of the first peak of polychloromethanes (10 mM) in DMF + 0.1 M Et$_4$NClO$_4$ recorded, at $v = 0.2$ V s^{-1}, in the absence and presence of 10-fold excess of acetic acid, HAc.

Compound	Without addition of HAc			With addition of HAc		
	$E_{p,GC}$[a]	$E_{p,Ag}$[a]	ΔE_p[b]	$E_{p,GC}$[a]	$E_{p,Ag}$[a]	ΔE_p[b]
CCl$_4$	−1.558	−1.549	0.009	−1.558	−1.008	0.550
CHCl$_3$	−2.163	−1.789	0.374	−2.187	1.354	0.833
CH$_2$Cl$_2$	−2.728	−2.225	0.503	−2.747	−2.150	0.597
CH$_3$Cl	−2.931	−2.051	0.882		−1.971	

[a] In V vs. SCE; $E_{p,Ag}$ and $E_{p,GC}$ are peak potentials measured at Ag and GC, respectively.
[b] $\Delta E_p = E_{p,Ag} - E_{p,GC}$.

The intermediate radical $^\bullet$CH$_n$Cl$_{(3-n)}$, being more easily reducible than the parent CH$_n$Cl$_{(4-n)}$ molecule, is immediately reduced to CH$_n$Cl$_{(3-n)}^-$, which is rapidly protonated by the added acid. The overall reaction mechanism could be exemplified as consecutive hydrogenolysis steps, occurring at increasingly more negative potentials, all of which involve reduction of the halogenated species along with loss of Cl$^-$ followed by reduction of the radical to the corresponding anion and subsequent protonation. The hydrogenolysis cyclically repeats itself until all Cl atoms are substituted by H atoms and methane is formed.

If a good proton donor is not added into the solution, other reactions of CH$_n$Cl$_{(3-n)}^-$, such as a father–son reaction with CH$_n$Cl$_{(4-n)}$ and dehalogenation leading to a carbene, become more important than protonation by the residual water or background electrolyte. This circumstance makes the reaction mechanism quite complex, and, above all, leads to a significant decrease of the selectivity of the hydrodehalogenation process. As a consequence, the intensity of the reduction peaks decreases progressively from the first to the last, especially for CCl$_4$ and CHCl$_3$.

Fig. 2 shows cyclic voltammetry of all four chlorinated methanes at a silver electrode both in the absence and presence of acetic acid. CCl$_4$ and CHCl$_3$ exhibit three and two irreversible reduction peaks, respectively, whereas both CH$_2$Cl$_2$ and CH$_3$Cl show a single reduction peak. E_p values of the first reduction process for each compound are summarized in Table 1. It is worth noting that E_p of chloromethane is slightly more positive than that of dichloromethane. Therefore, a separate peak cannot be observed for CH$_3$Cl starting from anyone of the more chlorinated compounds. Both CCl$_4$ and CHCl$_3$ give a first reduction peak, which is much higher in current than the other peaks. Addition of acetic acid enhances all reduction peaks. The mechanism of CH$_n$Cl$_{(4-n)}$ reduction at Ag is more complex than at GC owing to interactions of Ag with the substrate and its reduction intermediates and products [36]. However, as on the GC electrode, each compound is reduced in sequential steps that involve reduction of all the less chlorinated methanes as intermediate products and therefore similar considerations could be made. In particular, in the presence of a strong acid, each reduction peak represents an overall 2e$^-$ process leading to hydrodehalogenation of a carbon–chlorine bond according to reactions (1)–(3). The only exception is the peak at ca. −2.2 V vs. SCE for CCl$_4$, CHCl$_3$ and CH$_2$Cl$_2$, which involves concurrent reduction of the two least chlorinated compounds of the series.

The most important difference between the voltammetric responses at the two electrodes is a remarkable positive shift of all reduction peaks at Ag with respect to GC. This effect is ascribable to the extraordinary electrocatalytic properties of Ag, which has already been highlighted for the reduction of other organic halides [23–28]. The first peak potential of CCl$_4$ appears to be little affected by the nature of the electrode material ($E_{p,Ag} - E_{p,GC} = 0.009$ V). This may lead to the erroneous conclusion that there is no appreciable electrocatalysis for the reduction of CCl$_4$ at Ag. In fact, a
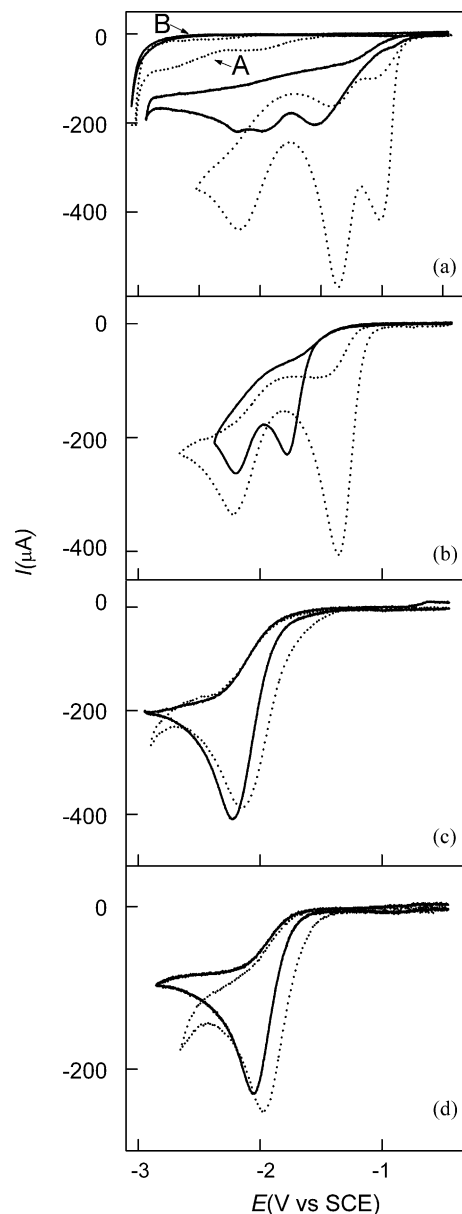

Fig. 2. Cyclic voltammetry of (a) 10 mM CCl$_4$, (b) 10 mM CHCl$_3$, (c) 10 mM CH$_2$Cl$_2$ and (d) 6 mM CH$_3$Cl recorded at $v = 0.2$ V s^{-1} at Ag in DMF + 0.1 M Et$_4$NClO$_4$ in the absence (solid line) and presence (dotted line) of 100 mM CH$_3$CO$_2$H; curves (B) and (A) stand for the background electrolyte and 10 mM CH$_3$CO$_2$H, respectively.

close inspection of the voltammograms at the two electrodes (Figs. 1b and 2b) reveals that, although the two processes have similar peak potentials, reduction at Ag commences at much more positive potentials than at GC. For example, at −1.0 V vs. SCE the current density at Ag is 10 times greater than at GC. Interestingly, the electrocatalytic activity of Ag is further enhanced by the presence of acetic acid, which shifts the reduction peaks to more positive potentials (see Table 1). This makes Ag a promising electrode material for the hydrodehalogenation of polychloromethanes under mild conditions.

3.2. Controlled-potential electrolyses

It is widely reported in the literature that reductive dechlorination of CCl$_4$ and CHCl$_3$ to CH$_4$ can be achieved in aqueous solutions by electrolysis [7,8,10,11,14] or by chemical reduction at

Table 2
Electrolysis of polychloromethanes (10 mM) in DMF + 0.1 M Et$_4$NClO$_4$ at a graphite cathode.

	E_{app}[a] (V)	n (F/mol)	CCl$_4$ (%)	CHCl$_3$ (%)	CH$_2$Cl$_2$ (%)	CH$_3$Cl (%)	CH$_4$ (%)	Total (%)[b]	Current efficiency (%)[c]
CCl$_4$	−1.9	3.0	13.3	21	7.7	0	2.3	44	30
	−2.3	4.3	0.8	3.8	4.8	0	15.4	25	35
	−2.9	5.6	0	0.3	1.1	0	23	24	34
CCl$_4$ + HAc[d]	−1.9	2.7	15.7	70	8.8	0	0.7	95	67
	−2.3	5.7	0.8	5.4	60	0.3	7.2	74	54
	−2.9	8.2	0	0	6.1	0.3	66	72	68
CHCl$_3$	−2.3	2.3		4.0	24	1.2	6.6	36	40
	−2.9	4.0		0	4.0	0.5	26	30	42
CHCl$_3$ + HAc[d]	−2.3	3.7		14	68	3.9	14	100	64
	−2.9	8		2.0	10.0	0.2	88	100	69
CH$_2$Cl$_2$	−2.9	2.0			47	5.0	17	69	39
	−2.9	4.0			0.4	0.1	39	40	39
CH$_2$Cl$_2$ + HAc[d]	−2.9	2.6			48	5.3	47	100	76
	−2.9	5.3			0	2.1	96	98	73
CH$_3$Cl	−2.9	2.0				0	97	97	97

[a] Applied potential vs. SCE.
[b] Mass balance for C$_1$ compounds with respect to initial substrate.
[c] Total current efficiency for all products considering a charge consumption of 2e$^-$, 4e$^-$, 6e$^-$ and 8e$^-$/molecule for the formation of CHCl$_3$, CH$_2$Cl$_2$, CH$_3$Cl and CH$_4$, respectively.
[d] In the presence of 50 mM CH$_3$CO$_2$H.

iron or its oxides [37–40]. The mechanism of this hydrodehalogenation process is not well established yet. In particular, there is no clear evidence that the process involves sequential dehalogenation steps leading to the intermediate formation of partially dechlorinated compounds. In some cases, it is assumed that CH$_2$Cl$_2$ and CH$_3$Cl are not even significant intermediates in the formation of CH$_4$ during the reduction of CCl$_4$ and CHCl$_3$ and, therefore, other reaction pathways are considered [15,40]. However, as evidenced by the voltammetric data in DMF, especially in the presence of an acid, it is possible to reduce selectively CCl$_4$ and all less chlorinated compounds arising from its reduction down to CH$_3$Cl, by operating under potentiostatic conditions.

The results of preparative-scale electrolyses of CCl$_4$, CHCl$_3$ and CH$_2$Cl$_2$ performed at graphite and silver cathodes, both in the absence and presence of HAc, are summarized in Tables 2–4. All experiments were conducted under potentiostatic conditions, but the applied potential was periodically shifted to more negative values during the experiment in order to reduce selectively one by one the starting compound and its reduction products. All experiments were interrupted after the current decreased to ca. 5% of its initial value, which often corresponded to a reagent conversion >95%.

Fig. 3 shows variations of the principal reduction products of CCl$_4$ together with cyclic voltammograms recorded during preparative electrolyses of the chloride at a graphite cathode. The cyclic voltammograms show degradation of CCl$_4$ with time as electrolysis proceeds and charge passed increases. Also the concentration trends of all products observed both in the solution and gas phases are illustrated in the figure. The electrolyses were carried out at three different applied potentials, namely

Table 3
Electrolysis of polychloromethanes (10 mM) in DMF + 0.1 M Et$_4$NClO$_4$ at a silver cathode.

	E_{app}[a] (V)	n (F/mol)	CCl$_4$ (%)	CHCl$_3$ (%)	CH$_2$Cl$_2$ (%)	CH$_3$Cl (%)	CH$_4$ (%)	Total (%)[b]	Current efficiency (%)[c]
CCl$_4$	−1.3	2.0	49	35	1.2	0	0.1	85	38
	−1.6	2.9	27	4.5	22	0	1.5	55	38
	−2.2	3.5	0	0	1.2	0	11.5	13	28
CCl$_4$ + HAc[d]	−1.0	3.7	20	69	0	0	7.4	96	53
	−1.4	6.4	3.2	15	21	0	50	89	80
	−2.2	8.6	0.8	3.2	5.9	0	81	91	79
CHCl$_3$	−1.6	1.9		12	65	0	5.8	83	87
	−2.2	3.7		0	3.6	0	36	40	60
CHCl$_3$ + HAc[d]	−1.4	4.6		8.1	27	0	64	99	95
	−2.2	8.6		0	0	0	97	97	68
CH$_2$Cl$_2$	−2.2	4.0			24	0	59	83	59
	−2.2	5.8			0	0	80	80	55
CH$_2$Cl$_2$ + HAc[d]	−2.2	4.0			47	0	53	100	53
	−2.2	8.0			3.0	0	97	100	49
CH$_3$Cl	−2.2	1.7				0	100	100	118

[a] Applied potential vs. SCE.
[b] Mass balance for C$_1$ compounds with respect to initial substrate.
[c] Total current efficiency for all products considering a charge consumption of 2e$^-$, 4e$^-$, 6e$^-$ and 8e$^-$/molecule for the formation of CHCl$_3$, CH$_2$Cl$_2$, CH$_3$Cl and CH$_4$, respectively.
[d] In the presence of 100 mM CH$_3$CO$_2$H.

Table 4
Electrolysis of 10 mM CCl$_4$ in DMF + 0.1 M Et$_4$NClO$_4$ at graphite and Ag cathodes.

Entry	Electrode	E_{app}[a] (V)	n (F/mol)	CCl$_4$ (%)	CHCl$_3$ (%)	CH$_2$Cl$_2$ (%)	CH$_3$Cl (%)	CH$_4$ (%)	Total (%)[b]	Current efficiency (%)[c]
1	Graphite	−2.9	4.6	0	1.5	0	0	6.8	8.3	12
2[d]	Graphite	−2.9	8	0	0	6.8	3	80	90	86
3	Silver	−2.2	3.8	1.2	0.6	0	0	16	18	34
4[e]	Silver	−2.2	9.3	0	0	0	0	92	92	79

[a] Applied potential vs. SCE.
[b] Mass balance for C$_1$ compounds with respect to initial substrate.
[c] Total current efficiency for all products considering a charge consumption of 2e$^-$, 4e$^-$, 6e$^-$ and 8e$^-$/molecule for the formation of CHCl$_3$, CH$_2$Cl$_2$, CH$_3$Cl and CH$_4$, respectively.
[d] In the presence of 50 mM CH$_3$CO$_2$H.
[e] In the presence of 100 mM CH$_3$CO$_2$H.

E_{app} = −1.90, −2.30 and −2.90 V vs. SCE, corresponding to the reduction of CCl$_4$, CHCl$_3$ and CH$_2$Cl$_2$, respectively. Conversion of CCl$_4$, as well as production of partially dechlorinated compounds, was monitored by cyclic voltammetry (Fig. 3a and d). Based on voltammetric responses, the applied potential was always changed when the concentration of the species mainly undergoing reduction dropped to less than 20% of its starting value. This rule was not applied in the last stage of the electrolysis, which was made almost exhaustive, a complete stop being carried out after the current has dropped to <5% of its initial value. As can be clearly seen, the product distribution depends strongly on the applied potential, E_{app}, as well as on the proton availability of the medium. In the absence of an added acid, when electrolysis of CCl$_4$ is performed at E_{app} = −1.9 V vs. SCE, where only CCl$_4$ is reducible, CHCl$_3$ is obtained as the main reduction product. Similarly, when the electrolysis potential is shifted to E_{app} = −2.3 V vs. SCE, where reduction of CHCl$_3$ occurs, CH$_2$Cl$_2$ and CH$_4$ become the principal reduction products. Eventually, at reduction potentials beyond E_p of CH$_2$Cl$_2$, E_{app} = −2.9 V vs. SCE, only methane is formed; CH$_3$Cl is detected only at a trace level. It is worth noting that when almost 90% of CCl$_4$ is converted at E_{app} = −1.90 V vs. SCE, only 21% CHCl$_3$, together with 8% CH$_2$Cl$_2$ and 2% CH$_4$, is obtained. Likewise, when

Fig. 3. Sequential electrolysis of 10 mM CCl$_4$ in DMF + 0.1 M Et$_4$NClO$_4$ at graphite electrode in the absence (a–c) and presence (d–f) of 50 mM CH$_3$CO$_2$H: (a, d) cyclic voltammograms of CCl$_4$ recorded during electrolysis with increasing charge consumption; (b, e) appearance of intermediates/products (n_s) in solution: (▲) CCl$_4$, (○) CHCl$_3$, (△) CH$_2$Cl$_2$, (●) CCl$_4$ + CHCl$_3$ + CH$_2$Cl$_2$; (c, f) appearance of intermediates/products (n_s) in the gaseous phase: (◇) CH$_3$Cl, (□) CH$_4$. The numbers stand for E_{app} in V vs. SCE and the vertical lines delimit the zone to which each E_{app} refers.

complete conversion of CCl$_4$ and all its reduction intermediates is achieved (3rd stage of the electrolysis) only 23% CH$_4$ is produced.

The results of electrolysis of CCl$_4$ at graphite in DMF containing acetic acid are reported in Fig. 3d–f and in Table 2. As compared to the electrolysis performed without added acid, much higher yields of all hydrodehalogenated compounds and a significantly better carbon mass balance are obtained in the presence of 0.1 M HAc. When the electrolysis of CCl$_4$ is carried out at −1.90 V vs. SCE, CHCl$_3$ is formed as the principal reduction product, its yield reaching 70% after 84% of CCl$_4$ has reacted; also CH$_2$Cl$_2$ is formed as a byproduct with a maximum yield of 9%. Formation of CH$_4$ at this potential is limited to a trace level, while production of CH$_3$Cl was below the detection limit. On the subsequent electrolysis step at E_{app} = −2.3 V vs. SCE, reduction of CHCl$_3$, mainly to CH$_2$Cl$_2$, occurs along with the reduction of the remaining CCl$_4$. At this stage, formation of CH$_4$ increases significantly, while trace amounts of CH$_3$Cl appear. When, at the end of this stage, the applied potential is shifted to −2.9 V vs. SCE, CH$_2$Cl$_2$ is almost quantitatively reduced to CH$_4$.

Electrolyses of CHCl$_3$ and CH$_2$Cl$_2$ at graphite show similar trends as those described for CCl$_4$. At E_{app} = −2.30 V vs. SCE, CHCl$_3$ is mainly reduced to CH$_2$Cl$_2$, which is then transformed into CH$_4$ at the second stage of the electrolysis performed at −2.90 V vs. SCE. As in the case of CCl$_4$, the yields of hydrodehalogenated compounds and the overall carbon mass balances are quite low if the experiment is carried out without added acid. If, instead, the electrolysis is performed in the presence of excess acetic acid, the sequential hydrodechlorination of CHCl$_3$ gives good yields of CH$_2$Cl$_2$ in the first step and of CH$_4$ in the second one. Direct electrolysis of CH$_2$Cl$_2$ at −2.9 V vs. SCE yields 39% CH$_4$, which increases to 96% in the presence of HAc.

The results of sequential step potentiostatic electrolyses of polychloromethanes at Ag are summarized in Table 3, whereas Fig. 4 illustrates, as an example, the trends of product concentrations during electrolysis of CCl$_4$, carried out both in the absence and presence of excess HAc. These data are qualitatively similar to the results obtained from the analogous experiments performed at the graphite cathode. However, a very important difference between the two electrode materials is that Ag possesses extraordinary electrocatalytic properties so that reduction of polychloromethanes at this electrode can be carried out at potentials ca. 0.6 V more positive than at graphite. Also better product distribution and higher overall mass balances are obtained at Ag than at graphite. As clearly shown in Fig. 4 and Table 3, electrolysis of CCl$_4$ at Ag at E_{app} = −1.30 V vs. SCE yields mainly CHCl$_3$, which in turn is transformed into CH$_2$Cl$_2$ at −1.60 V vs. SCE. The last step of the electrolysis at −2.20 V vs. SCE, where both CH$_2$Cl$_2$ and CH$_3$Cl are reduced, yields CH$_4$ as the principal product. Note, however, if no acid is added into the solution, the overall yield of CH$_4$ after total conversion is only 12%. This yield increases considerably when CHCl$_3$ and CH$_2$Cl$_2$ are electrolyzed directly at −1.60 and −2.20 V vs. SCE, respectively. In such cases, CH$_4$
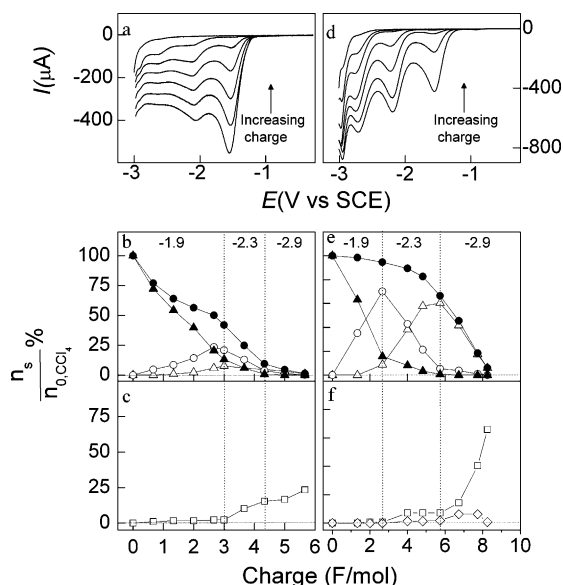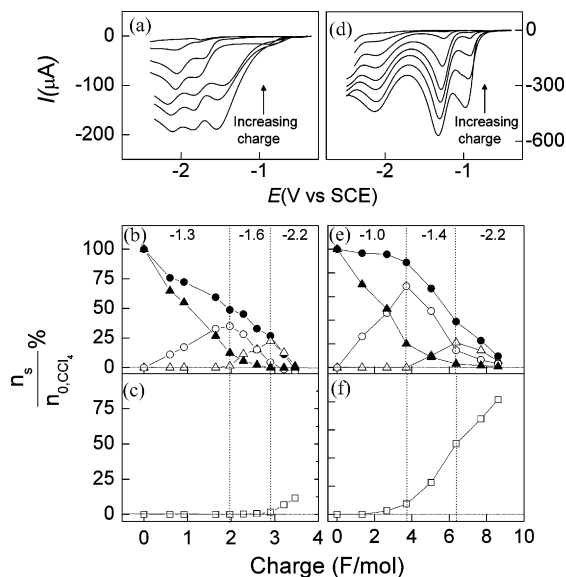
Fig. 4. Sequential electrolysis of 10 mM CCl_4 in DMF + 0.1 M Et_4NClO_4 at Ag electrode in the absence (a–c) and presence (d–f) of 100 mM CH_3CO_2H: (a, d) cyclic voltammograms of CCl_4 recorded during electrolysis with increasing charge consumption; (b, e) appearance of intermediates/products (n_s) in solution: (▲) CCl_4, (○) $CHCl_3$, (△) CH_2Cl_2, (●) $CCl_4 + CHCl_3 + CH_2Cl_2$; (c, f) appearance of intermediates/products (n_s) in the gaseous phase: (□) CH_4. The numbers stand for E_{app} in V vs. SCE and the vertical lines delimit the zone to which each E_{app} refers.

Fig. 5. Product distribution during electrolysis of 10 mM CCl_4 in DMF + 0.1 M Et_4NClO_4 at (a) graphite electrode, E_{app} = −2.90 V vs. SCE and (b) Ag electrode, E_{app} = −2.20 V vs. SCE: (○) $CHCl_3$, (△) CH_2Cl_2, (□) CH_4.

yields reaching 36% and 80% are obtained from $CHCl_3$ and CH_2Cl_2, respectively. When the electrolyses are performed in the presence of acetic acid, almost complete conversion of all chlorinated methanes to CH_4 is observed. The yields of CH_4 obtained from sequential electrolyses, where applicable, of CCl_4, $CHCl_3$ and CH_2Cl_2 at −1.0, −1.40 and −2.20 V vs. SCE were 81%, 97% and 100%, respectively.

To complete the series of the preparative-scale experiments on the reductive cleavage of chlorinated methanes, electrolysis of CH_3Cl was performed at graphite and Ag electrodes at −2.90 and −2.2 V vs. SCE, respectively. The experiments were performed without added acid and, as shown in Tables 2 and 3, almost quantitative conversion of CH_3Cl to CH_4 was observed on both electrodes.

The above results show that CCl_4 or any other polychloromethane can be sequentially reduced to less chlorinated methanes and ultimately to CH_4 by appropriately choosing the applied potential. If the goal is to convert CCl_4 to CH_4, a single step potentiostatic electrolysis may be more appropriate than a multi-step electrolysis. Some electrolyses of CCl_4 were carried out at graphite and Ag electrodes at fixed potentials of −2.90 and −2.20 V vs. SCE, respectively (Table 4). The results of these electrolyses are very similar to those obtained from multi-step potentiostatic experiments, both in terms of CH_4 yield and charge consumption. However, one step electrolysis has the advantage of working with higher current densities as compared to multi-step electrolyses and hence the experiment lasts in a much shorter time. As in the multi-step experiments, the concentrations of all intermediates as well as that of methane depend on the charge consumed during electrolysis. These variations are illustrated in Figs. 5 and 6. The concentrations of $CHCl_3$ and CH_2Cl_2 increase in the first part of the electrolysis, but decrease, approaching zero, in the second part of the experiment. In addition, the curve for CH_2Cl_2 reaches its maximum later than that of $CHCl_3$. The shapes of these curves point out that formation of these intermediates takes place through a reaction sequence in which the Cl atoms are removed one at a time until methane is obtained.
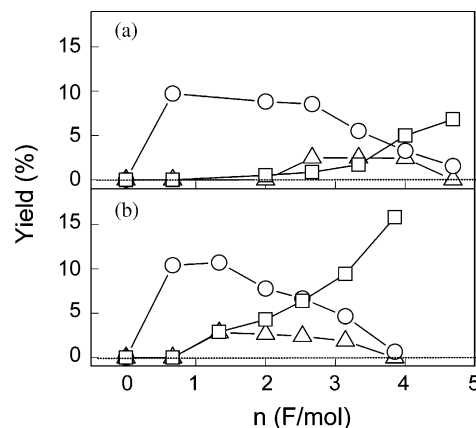
A last comment on these one step potentiostatic electrolyses is on the production of methane. As shown in Fig. 5, the yield of CH_4 is quite low (<16%) when no acid is added into the reaction medium. Conversely, when the electrolysis is performed in the presence of acetic acid, very high yields of CH_4 are obtained (Fig. 6). It is worth noting that a slight, albeit significant, difference between the two electrode materials can be observed for the formation of this product. At both electrodes, production of CH_4 starts at the beginning of the electrolysis. However, at graphite the yield of the hydrocarbon increases very slowly in the first three quarters of the electrolysis, but rises steeply in the last part of the experiment. In contrast, at Ag production of CH_4 increases steadily during the whole of the experiment, especially in the presence of acetic acid. It appears that Ag promotes formation of CH_4 without necessarily accumulating first the partially dechlorinated compounds.

According to the results reported so far, the leading path for the reductive cleavage of polychloromethanes at both electrodes appears to be sequential hydrodechlorination leading to the formation of methane. However, the mass balance is well below 100% in several cases, especially if a good proton donor is not present in solution. In view of this, we looked for other possible reduction products such as chlorinated or non-chlorinated ethanes and ethylenes as well as higher molecular weight hydrocarbons. With the exception of tetrachloroethylene, which was found at
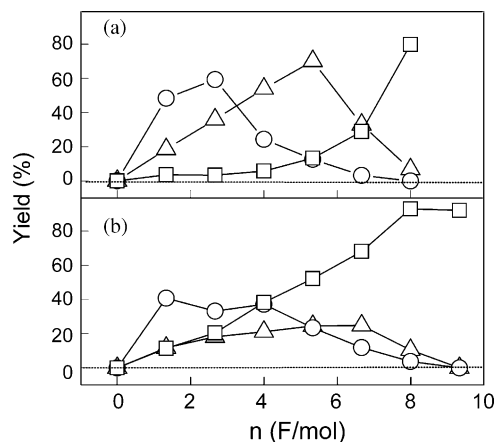

Fig. 6. Product distribution during electrolysis of 10 mM CCl_4 in DMF + 0.1 M Et_4NClO_4 at (a) graphite electrode in the presence of 50 mM CH_3CO_2H, E_{app} = −2.90 V vs. SCE and (b) Ag electrode in the presence of 100 mM CH_3CO_2H, E_{app} = −2.20 V vs. SCE: (○) $CHCl_3$, (△) CH_2Cl_2, (□) CH_4.

trace levels ($<1\%$) only on Ag, no chlorinated compounds could be observed under any circumstances. In addition, higher molecular weight hydrocarbons presumably arising from telomerization or polymerization of intermediates were never detected. On the other hand, analysis of chloride ions at the end of the electrolysis, confirmed complete dechlorination of the starting polychloromethane.

Concerning the non-chlorinated C2 compounds, ethylene was detected at both electrodes, in some cases even in large amounts. There are, however, several lines of evidence that the principal source of this product is not the starting polychloromethane or its reduction intermediates. First, if ethylene is taken into account in the carbon mass balance, overall yields well beyond 100% are observed in some cases. For example, electrolysis of CH_2Cl_2 at Ag gives 80% CH_4 and 172% C_2H_4, which sum up to 252%. Second, formation of C_2H_4 steadily increases with CH_4 production (see Fig. 7). Now starting from any polychloromethane, we could envisage that formation of C2 compounds involves radical coupling reactions, whereas methane formation requires hydrodechlorination reactions. Since these two reaction paths are in competition, simultaneous increase of CH_4 and C_2H_4 is an unreasonable result, suggesting that C_2H_4 does not arise directly from reduction of polychloromethanes. Finally, we observed that C_2H_4 production decreases drastically when the same electrolyses are repeated in the presence of acetic acid (Fig. 7). This fact, together with the simultaneous increase of CH_4 and C_2H_4 concentrations, suggests that C_2H_4 arises from Hoffmann degradation of tetraethylammonium ions. It is well known that R_4N^+ reacts readily with strong bases such as OH^- to give trialkylamines and olefins [41–43]. Thus, $(C_2H_5)_4N^+$ could react with hydroxide ions arising from protonation of $CH_nCl_{(3-n)}^-$ by residual water or directly with the electrogenerated carbanions to give ethylene as shown by Eq. (4) in the case of OH^-.

$$(C_2H_5)_4N^+ + OH^- \rightarrow CH_2=CH_2 + (C_2H_5)_3N + H_2O \qquad (4)$$
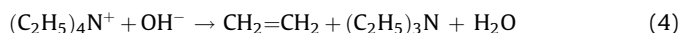
To check this possibility, we performed some experiments using $(C_4H_9)_4NClO_4$ as supporting electrolyte. As expected, production of C_2H_4 was not observed in these experiments.
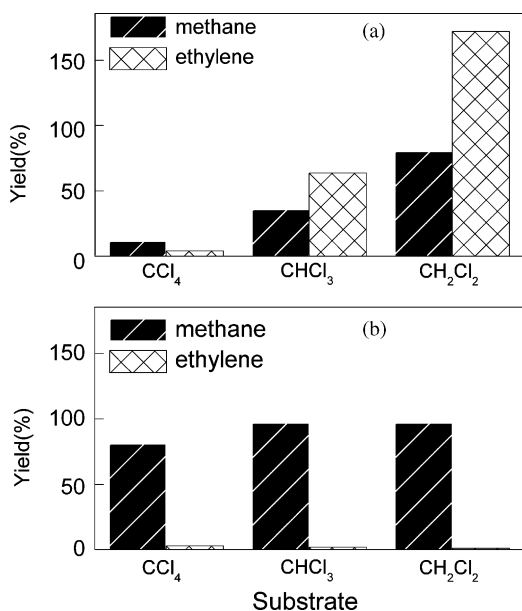

Fig. 7. Exhaustive electrolysis of polychloromethanes in DMF + 0.1 M Et_4NClO_4 at Ag in the absence (a) and presence (b) of CH_3CO_2H.

3.3. Mechanistic considerations

Reduction of chlorinated methanes ($CH_nCl_{(4-n)}$, $n = 0$–3) at carbon and silver electrodes in DMF yields methane as the principal product. The process occurs through a series of reduction steps each involving two electron transfers, removal of a chloride ion and protonation (Scheme 1). Thus, starting from CCl_4 a concerted dissociative electron transfer yields a trichloromethyl radical and a chloride ion; this is followed by $1e^-$ reduction of the radical and protonation of the ensuing carbanion to give chloroform. If the applied potential is negative enough to ensure electroreduction of all chlorinated methanes, the same pattern is repeated again and again until methane is formed, i.e., $CCl_4 \rightarrow CHCl_3 \rightarrow CH_2Cl_2 \rightarrow CH_3Cl \rightarrow CH_4$. Although this appears to be the most important reaction route, leading to high CH_4 production under favorable conditions, it is not the only possible reaction pathway. Indeed, low yields of CH_4 were obtained when the electrolyses were performed in the absence of a good proton donor. Therefore, other reaction pathways in competition with the hydrodechlorination sequence ought to be considered. These may involve either the radical $^\bullet CH_nCl_{(3-n)}$ or the carbanion $CH_nCl_{(3-n)}^-$ or both of them. Formation of C2 compounds arising from polychloromethanes was either detected at trace levels or was not detected at all. This rules out radical-radical coupling reactions as a relevant route for the decay of intermediate radicals. On the other hand, it is well established that the reductive cleavage of alkyl halides is a $2e^-$ process because the intermediate alkyl
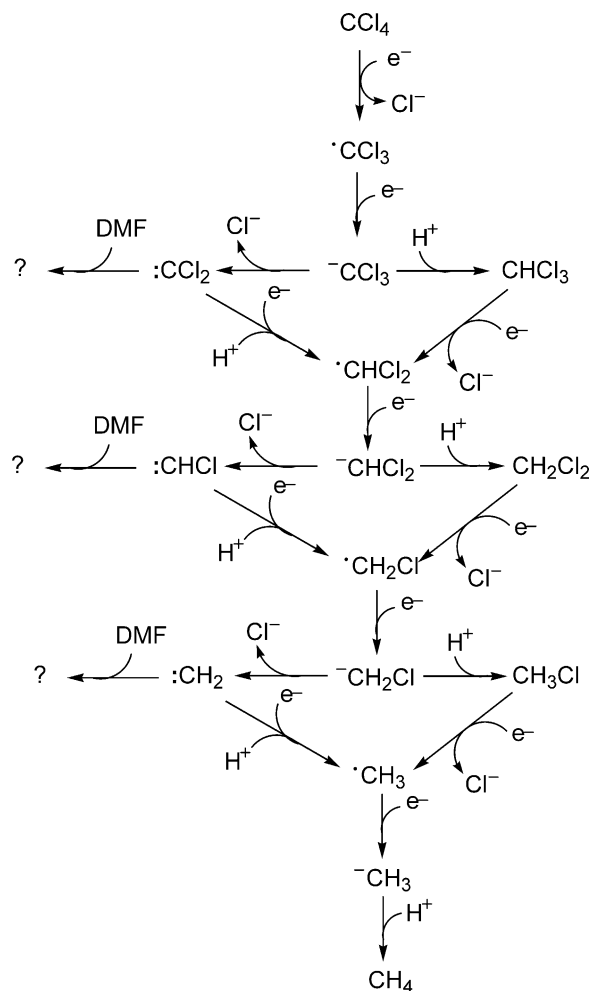
Scheme 1. Reaction scheme for the reduction of polychloromethanes.

radicals are more easily reducible than the parent alkyl chlorides [25,28,33].

A possible reaction of $CH_nCl_{(3-n)}^-$, in competition with protonation, is expulsion of Cl^- to give a carbene:

$$CH_nCl_{(3-n)}^- \rightarrow :CH_nCl_{(2-n)} + Cl^- \tag{5}$$

Formation of carbenes from polyhalomethyl carbanions by elimination of a halide ion is well documented in the literature [15,38,40,43–45]. Dihalocarbenes react rapidly with DMF to give CO and (dihalomethyl)dimethylamine [45]. It is also known that in aqueous solutions halocarbenes such as $:CCl_2$ readily undergo hydrolysis leading to the formation of carbon monoxide. However, in dry DMF hydrolysis is less likely than the reaction with the solvent. Although we have not investigated the fate of chlorocarbenes, we assume that polychloromethyl carbanions are partitioned into two parallel reactions, i.e., protonation (Eq. (3)) and Cl^- release (Eq. (5)). This competition is governed by the stability of the chlorinated methyl carbanion and the proton availability of the medium. In the absence of any added acid, a significant fraction of $CH_nCl_{(3-n)}^-$ undergoes dechlorination to give a carbene and hence the overall yield of CH_4 is not very high. When acetic acid is added into the solution, reaction (3) becomes much faster than chloride ion loss, resulting in very high yields of hydrodehalogenation products.

There are some results in contrast with the above described mechanism based on the competition between two reaction routes, one leading to CH_4 and the other yielding unidentified products arising from reaction of carbenes with DMF. Formation of CH_4 through sequential hydrodechlorination (Eqs. (1)–(3)) of any polychloromethane implies the intermediate production of all less chlorinated methanes. Nevertheless, as shown in Tables 2–4, this has not always been observed. Indeed, intermediate formation of CH_3Cl was observed during electrolyses at graphite, but its maximum yield rarely exceeded 5% even in experiments where ca. 100% conversion of the starting polychloromethane to CH_4 was achieved. The result is more striking at Ag where CH_3Cl formation was never observed. This discrepancy is possibly due to the fact that the reduction potential of CH_3Cl at Ag is more positive than that of CH_2Cl_2, so that CH_3Cl is converted to CH_4 as soon as it is formed. In contrast, the reduction potential of CH_3Cl at graphite is slightly more negative than that of CH_2Cl_2; therefore, some CH_3Cl survives reduction at the applied potential for CH_2Cl_2 reduction (E_{app} = −2.90 V vs. SCE).

Also a careful analysis of the yield of CH_4 gives a clear evidence that sequential hydrodehalogenation (Eqs. (1)–(3)) cannot fully account for its production. Sequential hydrodehalogenation of $CH_nCl_{(4-n)}$ to CH_4 not only requires the intermediacy of all possible chlorinated methanes but also working potentials around the reduction potential of CH_3Cl. This means that, in principle, electrochemical conversion of $CH_nCl_{(4-n)}$ to CH_4 can be achieved only if $E_{app} \leq -2.90$ V vs. SCE at graphite or $E_{app} \leq -2.10$ V vs. SCE at Ag. The data reported in this paper clearly contrast these predictions (Tables 2 and 3). The role of E_{app} on CH_4 yield is illustrated in Fig. 8, which reports data obtained from electrolysis of CCl_4 in different operating conditions. When graphite electrode is used, a small amount of CH_4 is obtained at −1.90 V vs. SCE; this further increases as E_{app} is shifted to −2.30 and to −2.90 V vs. SCE. As mentioned earlier, these potentials correspond to the reduction of CCl_4, $CHCl_3$ and CH_2Cl_2, respectively. A similar trend is observed at Ag, but now the applied potentials are −1.30, −1.60 and −2.20 V vs. SCE. These results point out that CH_4 can be obtained from reduction of CCl_4 at potentials where electroreduction of all less chlorinated compounds is not possible. Similar results were obtained for the reduction of $CHCl_3$ and CH_2Cl_2 at both electrodes (see Tables 3 and 4). To check
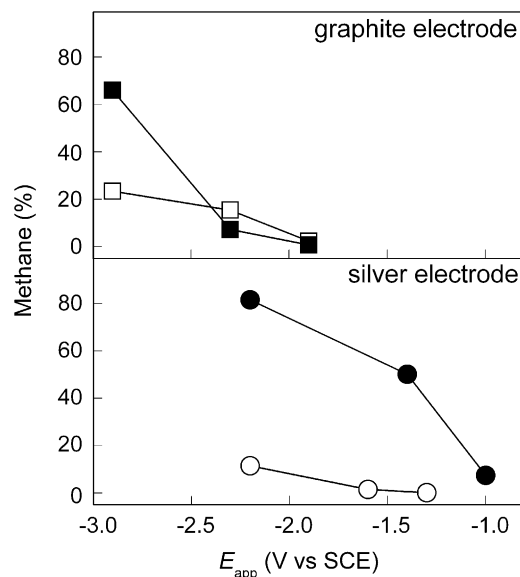

Fig. 8. Electrolysis of CCl_4 in DMF + 0.1 M Et_4NClO_4 at Ag ($\bullet$, $\circ$) and graphite ($\blacksquare$, $\square$) in the absence (empty symbols) and presence (full symbols) of CH_3CO_2H. Dependence of the yield of CH_4 on the applied potential.

whether formation of CH_4 follows a full sequence of hydrodehalogenation steps involving $CHCl_3$, CH_2Cl_2 and CH_3Cl or can bypass the intermediate formation of these compounds, some experiments were performed on each substrate at the above potentials. However, none of them produces methane by electrolysis at potentials more positive than its proper reduction potential; actually no current passes and no reduction occurs at all.

It is clear that, besides sequential hydrogenolysis, CH_4 is produced by a second reaction pathway which bypasses partially dechlorinated methanes as intermediates. A possible reaction route could be sequential hydrogenolysis involving carbenes, which has been previously proposed for the chemical reduction of CCl_4 to CH_4 at Fe and iron oxides [38,40]. For example, in the case of CCl_4 reactions (1), (2) and (5) give dichlorocarbene which may undergo the following sequence of reactions leading to CH_4:

$$:CCl_2 + e^- + H^+ \rightarrow {}^\bullet CHCl_2 \tag{6}$$

$${}^\bullet CHCl_2 + e^- \rightleftarrows CHCl_2^- \tag{7}$$

$$CHCl_2^- \rightarrow :CHCl + Cl^- \tag{8}$$

$$:CHCl + e^- + H^+ \rightarrow {}^\bullet CH_2Cl \tag{9}$$

$${}^\bullet CH_2Cl + e^- \rightleftarrows CH_2Cl^- \tag{10}$$

$$CH_2Cl^- \rightarrow :CH_2 + Cl^- \tag{11}$$

$$:CH_2 + e^- + H^+ \rightarrow {}^\bullet CH_3 \tag{12}$$

$${}^\bullet CH_3 + e^- \rightleftarrows CH_3^- \tag{13}$$

$$CH_3^- + H^+ \rightarrow CH_4 \tag{14}$$

Reduction of each carbene to the corresponding radical requires the transfer of $1e^-$ and one proton, which may occur either in a single step or in two successive steps. Since the precise mechanism of this hydrogenation reaction is not known, reactions (6), (9) and

(12) merely represent the overall process. Reduction of the neutral radical stemming from the proton–electron transfer to dichlorocarbene yields a dichloromethyl carbanion, which loses rapidly a chloride ion, thus generating a new carbene capable of starting a new cycle of hydrogenation, reduction and Cl^- elimination reactions.

The overall mechanism of electroreduction of polychloromethanes is depicted in Scheme 1. When a strong acid is not present in solution, self-protonation reactions involving $CHCl_3$ and CH_2Cl_2 should also be considered in the reaction mechanism. Since, however, these reactions do not introduce new products or intermediates but make the reaction scheme more complicated [36], they were omitted for the sake of clarity. As shown, two distinct reaction pathways both leading to CH_4 are considered; these are sequential hydrodehalogentaion (Scheme 1, right-hand side) and sequential hydrogenolysis of carbenes (left-hand side) and they have a series of radicals and carbanions in common. A third reaction pathway involves reaction of carbenes with the solvent. Dimerizations and polymerizations involving intermediate radicals and carbenes can be excluded by the absence of C2 or higher molecular weight compounds among the products. The competition between these reaction routes depends strongly on the proton availability of the medium as well as on the nature of the electrode material and on the applied potential. In particular, when no acid is added into the solution, reaction of carbenes with DMF becomes important with deleterious effects on the overall carbon mass balance (Tables 2–4). The effect of the experimental conditions on CH_4 yield is shown in Fig. 8, which reports data from electrolysis of CCl_4. If the applied potential is limited to the first reduction step, a very small amount of CH_4 is produced at either electrode, obviously via the carbene route since $CHCl_3$ and all less chlorinated methanes are not reducible in these conditions. The very small production of CH_4 suggests that at these potentials reduction of carbenes is quite slow. Shifting the applied potential to more negative values increases CH_4 production. In particular, at potentials of the second reduction step, where reduction involves CCl_4 and $CHCl_3$ but not CH_2Cl_2 and CH_3Cl, significant amounts of CH_4 arising from carbene reduction are obtained. Methane production increases further at the potentials of the last step, but at such potentials both reaction pathways contribute to its formation. The role of the acid is quite complex as both reaction routes require protons. When the carbene reaction channel is limited by reduction of carbenes at the electrode, addition of an acid is expected to have a little or a negative effect on CH_4 production because less carbene will be formed owing to the increased rate of protonation of the primary carbanion (reaction (3) vs. reaction (5)). This is what is observed at the graphite cathode.

The electrode material plays a very interesting role in the reductive destruction of polychloromethanes and, in particular, in the competition between the two reaction pathways leading to methane formation. Silver has powerful electrocatalytic properties for the reduction of carbon–halogen bonds, an effect probably stemming from the affinity of the metal for halide ions. The catalytic activity of Ag is often enhanced by the presence of acids, which probably accelerate the rate of regeneration of the active sites on the metal surface. Interactions of Ag with the starting compounds and most of their reduction intermediates and products, especially radicals, carbenes and chloride ions, will drastically affect the reaction mechanism. As compared to graphite, the process occurs at much more positive potentials with comparable performances for CCl_4 conversion to CH_4 when no acid is added into the solution. In contrast, when the electrolyses are carried out in the presence of acetic acid, very high CH_4 yields are obtained at Ag even at potentials where CH_2Cl_2 and CH_3Cl are not reduced (Fig. 8), clearly indicating that Ag favors the carbene reaction route. The experiments with $CHCl_3$ and CH_2Cl_2 provide a glaring evidence of this effect. Electrolyses of $CHCl_3$ and CH_2Cl_2 performed at graphite in the absence of acetic acid show CH_4 yields of 26% and 39%, respectively (Table 2). When the same electrolyses are repeated at Ag at considerably more positive potentials, the yields of CH_4 increase up to 36% and 80%, respectively (Table 3). It may be inferred from this comparison that the rate of carbene formation is higher at Ag than at graphite. Possibly the rate of elimination of Cl^- by CCl_3^- and all less stable carbanions is enhanced by interactions of Cl^- and carbenes with the Ag surface. Also electroreduction of the carbenes, especially in the presence of an acid (Eqs. (6), (9) and (12)), may be catalyzed by Ag.

4. Conclusions

Silver shows extraordinary electrocatalytic properties toward the reductive cleavage of C–Cl bonds in polychloromethanes. At both Ag and carbon electrodes polychloromethanes can be selectively reduced to less chlorinated methanes by appropriately choosing the reaction conditions. The process occurs according to two competing reaction pathways: sequential hydrodehalogenation involving formation of all less chlorinated compounds and hydrogenolysis via carbenes. This competition is strongly influenced by the proton availability of the medium and also by the nature of the electrode material. If a strong proton donor is added into the solution, sequential hydrodechlorination appears to be the principal reaction path at both electrodes. In these conditions controlled potential electrolysis at both electrodes gives high yields of methane without any passivation of the cathode, especially Ag.

The most important outcome of this study is that highly toxic chlorinated methanes can be converted to methane under fairly mild conditions and this certainly is a result of high environmental relevance as it affords the bases for developing reductive destruction methods in combination with physical removal of PCMs from contaminated wastewaters. Since these compounds are highly soluble in dipolar solvents such as DMF or acetonitrile, they could be transferred from the gas phase or solid phase adsorbants and successively electrolyzed at catalytic electrodes such as silver. Electrocatalytic reduction in organic solvents is particularly appropriate when huge quantities of PCMs are to be destroyed. This destructive electrochemical technology could be implemented at industrial sites where chlorinated VOCs are produced as byproducts in the synthesis of important industrial reagents such as, for instance, vinyl chloride.

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